Biological and geochemical records of human-induced eutrophication in a small hard-water lake

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In areas with a long history of urbanization and agriculture, ecological properties of lakes can be substantially altered by anthropogenic eutrophication. We used a paleolimnological approach to identify how anthropogenic change affected a hard-water lake ecosystem during the last 200 years. Using sedimentary pigments, green algal remains, pollen analyses and stable carbon and oxygen isotopes (δ13Ccarb and δ18Ocarb), we assessed the dynamics of paleo-indicators of eutrophication in Lake Verevi (southern Estonia) and compared these with historical evidence and limnological surveys. The study site was also selected to quantify the impact of a documented change in water level on sedimentary pigment preservation (via changes in oxygen and light availability) and green algal remains (whose abundance is higher in the littoral zone). In addition, the ratio of chlorophyll a to phycocyanin a provided valuable information on sedimentation conditions, and thus, helped interpret the variation in sedimentary pigments concentrations. All indicators showed a synchronous ecological response to an increasingly pronounced anthropogenic impact. Furthermore, our results showed that the first sign of eutrophication was present as early as the 19th century, as indicated by a sharp rise in green algae (Pediastrum), more positive δ13Ccarb values, and a pronounced increase in phytoplankton pigment concentrations. Pollen data showed that these changes coincided with land clearance and the start of agricultural activities. The δ13Ccarb and δ18Ocarb data were strongly correlated and enriched isotopic content coincided with the eutrophication signal.

Introduction

Cultural eutrophication is an increasing problem worldwide. It is therefore critical to understand within-lake processes associated with this change both across the landscape and through time (Smol 2008, Waters et al. 2009, Bennion et al. 2011), and better characterize how eutrophication dynamics differ among lake types. For instance, in hard-water lakes, eutrophication can be mitigated by co-precipitation of phosphorus with CaCO3 from the water column (Wetzel 2001). However, under prolonged stress, this internal buffer might not be sufficient to curtail further degradation, and ultimately, lake ecosystem may be altered significantly. Reaching this limit of resilience can lead to a drastic change in the functioning of lake ecosystems (Sayer et al. 2006, Scheffer et al. 2007).
One of the most important symptoms of eutrophication is the excess growth of planktonic algae and cyanobacteria. Algal blooms lead to a decline in water quality with multiple ecological and socio-economic consequences. Often, monitoring data are only available for a limited time period and do not provide a continuous record of change nor track the onset of human influence on lakes (Smol 2010). The paleolimnological approach can be used to describe past changes in the algal community, thus providing valuable information on the history of eutrophication that pre-dates lake monitoring (Hall and Smol 1999, Sayers et al. 2010, Battarbee et al. 2012, Moss 2012, Wiik et al. 2015).

As sedimentary pigments are derived mostly from phytoplankton, pigment analysis is an established technique used to study past changes in phytoplankton composition (Leavitt and Hodgson 2001, McGowan et al. 2005, Waters et al. 2005, McGowan et al. 2012). Indeed, numerous studies have demonstrated the reliability of sedimentary pigments in reconstructing changes in the phytoplankton community and production over time (Leavitt and Hodgson 2001, Waters et al. 2005, Mikomägi and Punning 2007).

In addition, there has been a substantial increase in studies reporting non-pollen palynomorphs as proxies for environmental change (Kramer et al. 2010, Cook et al. 2011). Some, such as the remains of the colonial green algae *Pediastrum* species, can be used to reconstruct ecosystem-level responses to external disturbances (Jankovská and Kovárek 2000, van Geel 2001). For instance, the rise in *Pediastrum* and *Botryococcus* remains in the sediment were found to faithfully track the rise in lake trophic status (Koff et al. 2005, Vandel and Koff 2011).

Lastly, isotopic analyses of carbon and oxygen have become an important tool in paleolimnological reconstructions (Kelts and Talbot 1989, Neumann et al. 2002, Leng et al. 2005). In hard-water lakes, algal photosynthesis in the epilimnion consumes CO₂, which increases the pH and initiates CaCO₃ precipitation (Hodell et al. 1998). The accumulating carbonates are enriched in ¹³C because phytoplankton and macrophytes preferentially use lighter ¹²CO₂ from lakes (McKenzie 1985, Dean 1999). Therefore, in lakes, where precipitation of authigenic carbonates is induced by the biological activity of surface waters, the values of δ¹³C in sedimentary carbonates are affected by phytoplankton productivity (Lu et al. 2010). Generally, the δ¹⁸O curve is a good indicator of past climate change (Anderson et al. 2001, Leng et al. 2005). However, eutrophication might affect the oxygen isotope record by enhancing CaCO₃ precipitation, resulting in a non-equilibrium fractionation effect (Fronval et al. 1995, Teranes et al. 1999). More work is need, in combination with other proxies, to improve the interpretation of this poorly-understood indicator.

The availability of historical and limnological survey data, which cover most of the last century, makes Lake Verevi an excellent study site to examine the response of the phytoplankton community to ongoing eutrophication. Indeed, numerous studies conducted over the last decade to examine the ecological status of the lake (Heinsalu and Alliksaar 2005, Kangro et al. 2005, Mäemets and Freiberg 2005, Nõges 2005, Nõges and Kangro 2005, Ott et al. 2005) were aimed at predicting the functioning of this lake and to determine the best method for its restoration. The objectives of this study were thus to (1) explore the applicability of several novel paleolimnological methods (sedimentary pigments, stable carbon and oxygen isotope ratios from carbonates and non-pollen palynomorphs) to define the temporal dynamics of eutrophication in a small hard-water lake, and (2) compare the paleo-indicator dynamics with historically recorded intensive human influence (population growth), increase in recreational activity and nutrient loading from a wastewater treatment plant. Furthermore, we hypothesized that a documented drop in the water level of Lake Verevi (0.7 m in 1998) led to a more important change in sedimentary pigment concentrations, relative to other paleo-indicators. More specifically, we hypothesized that the large decrease in water level led to unfavorable sedimentation conditions for sedimentary pigments (e.g. higher oxygen and light availability; Leavitt and Hodgson 2001), but had a relatively minor effect on the other proxies examined here. We expected the impact of this drop to be most pronounced in the littoral zone where water depth is lowest (2.1 m on average).
Study site

Lake Verevi (58°13´N, 26°24´E; Fig. 1) is a small, glacial lake located in the city of Elva, southern Estonia. The surface area is approximately 0.13 km², maximum and mean depths are of 11 m and 3.6 m, respectively, and the mean water residence time is < 1 year. It is a hard-water lake with total alkalinity (HCO₃⁻) during the 1957–2001 averaging 213.8 mg l⁻¹. In recent years, the lake has become hypereutrophic (average total phosphorus concentration documented by limnological surveys of 165.5 mg m⁻³) and partly meromictic (Ott et al. 2005). Hypolimnetic nutrient concentrations peaked in 2000, with total nitrogen and total phosphorus concentrations reaching ~13 000 mg m⁻³ and ~1500 mg m⁻³, respectively (Ott et al. 2005). Yearly primary productivity was on average 220 mg C m⁻² and highest (340 mg C m⁻² year⁻¹) in the mid-1990s (Nõges and Kangro 2005). Sedimentation processes in the littoral zone of Lake Verevi were evaluated and confirmed that most of the organic matter in the sediment is produced by algae (Vandel and Koff 2011).

The lake is divided into two basins: the southern basin is round and deep, whereas the northern basin is long, narrow and shallow and largely covered by submerged macrophytes (especially Ceratophyllum demersum; Mäemets and Freiberg 2005). Small irregular inlets, which are dry most of the year, are situated along the southern basin. The main outflow at the start of the Kavilda River is on the western shore. The catchment (surface area = 1.1 km²) is composed of sandy hills with pine forest and drained wetlands (Ott et al. 2005). The climate of the region is humid and temperate.

Material and methods

Sampling and chronology

Sediment cores were taken from the narrow and shallow north basin from a water depth of 2.1 m, using a modified Livingstone-Vallentyne piston corer. The sediment cores (V96 and V94) were collected during ice cover in February 2009. The cores (74 and 60 cm in length, respectively) were cut in the field into 2-cm sections and samples were packed in plastic boxes. The samples from the V96 core were flushed with argon and stored in the dark at 4 °C. Subsamples from this core to

Fig. 1. Location of the study site, Lake Verevi, and digital elevation model (DEM) of the catchment area. The black dot indicates the coring location.
be used for sedimentary pigment analysis were freeze-dried and stored at −20 °C prior to analysis, whereas subsamples used for other analyses (stable isotopes, pollen and non-pollen palynomorphs) were stored in the cold. Four samples from different depths were additionally analyzed by X-ray diffractometry (XRD) to identify dominant carbonate minerals. The XRD analysis was performed on Bruker D8 Advanced with the Rietveld method in TOPAS software in the Institute of Geology, Tallinn University of Technology. The V94 core was used for 137Cs- and 210Pb-dating by gamma-spectroscopy (conducted by Gennady V. Laptev at the Ukraine Hydrometeorological Research Institute). The sediment core chronology was determined using the Constant Rate of Supply (CRS) model (Appleby and Oldfield 1978). Both cores were analyzed for loss on ignition (LOI) according to standard methods (Boyle 2000, Boyle 2001, Heiri et al. 2001). The organic matter (OM) and CaCO3 contents were estimated by igniting the samples at 550 °C (4 h) and 950 °C (2 h 30 min), respectively. The two cores were matched by their loss on ignition profiles.

Lake water samples for stable isotope analysis were collected from the top and bottom water layers of the pelagic and littoral zones of the lake in the spring (March 2009), autumn (October 2011) and summer (June 2013) months when the water column was stratified. Water samples from the lake inflow were collected in October 2011 (Table 1).

### Sedimentary pigments

Sedimentary pigments were analyzed at the Institute of Ecology at Tallinn University. Pigments were extracted from approximately 200 mg of freeze-dried sediments in acetone for 24 h at 4 °C. The pure extracts were dried by flushing the samples with N2. Samples were then spun in a refrigerated centrifuge and the supernatant was decanted, filtered (0.2 µm) and placed in vials for analysis with a Perkin Elmer high performance liquid chromatography (HPLC) system with Lichrosorb RP-18 column (5 µm particle size; 250 mm × 4.6 mm i.d.) and UV-VIS. For better resolution, an ion-pairing reagent was added to solvent A (Mantoura and Llewellyn 1983), which consisted of methanol, water and IPR solution (80:10:10). Solvent B included acetone and methanol (60:40). The gradient program with the total run time of 72 min was applied with a detection wavelength of 435 nm (Leavitt and Hodgson 2001). We separated and identified pigments of different taxonomic origin using the retention times of known standards (DHI, Hoersholm, Denmark). All algae and plants [chlorophyll a (Chl a), β-carotene], total cyanobacteria (echinenone), colonial cyanobacteria (canthaxanthin) and chlorophytes [chlorophyll b (Chl b)] were quantified (Leavitt and Hodgson 2001, Bianchi et al. 2002, McGowan et al. 2005, Choudhary et al. 2010). We also measured the stable Chl a degradation product, pheophytin a, and the ratio of labile Chl a to stable pheophytin a to track changes in pigment preservation throughout the core. Co-eluted pigments such as lutein and zeaxanthin were not divided but instead considered to be a complex of chlorophytes and cyanobacteria (Leavitt and Hodgson 2001). Pigment values are given in the HPLC units, g⁻¹ OM.

### Pollen and non-pollen palynomorphs

Pollen and non-pollen palynomorphs analyses
were conducted on 1-cm³ samples following standard pollen preparation methods (Moore et al. 1991, van Geel 2001). Green algae remains (Pediastrum spp.) were enumerated on pollen slides and identified following descriptions and illustrations in van Geel (2001). Pollen relative abundances were calculated based on total terrestrial pollen, and pollen diagram constructed using the TILIA and TGView computer programs (Grimm 1993, 2004).

Stable carbon and oxygen isotopes

Stable isotope analysis was performed at the Institute of Geology at Tallinn University of Technology. Stable isotopes from sediments ($\delta^{13}$C$_{\text{carb}}$, $\delta^{18}$O$_{\text{carb}}$), $\delta^{13}$C from lake-water dissolved inorganic carbon ($\delta^{13}$C$_{\text{DIC}}$) were analyzed using a Thermo Fisher Scientific mass spectrometer Delta V Advantage and GasBench II preparation line. Sediment samples were homogenized prior to analysis. Stable carbon and oxygen isotope composition were determined from carbon dioxide by decomposing the samples in 100% phosphoric acid at 70 °C. Results of $\delta^{13}$C$_{\text{carb}}$ and $\delta^{13}$C$_{\text{DIC}}$ are reported using the standard $\delta$-notation per mil (‰) on the VPDB (Vienna Pee Dee Belemnite) scale. The reproducibility of our results is ±0.1‰ for carbonates and ±0.5‰ for $\delta^{13}$C$_{\text{DIC}}$. The stable oxygen isotopes and hydrogen isotopes from lake water ($\delta^{18}$O$_{\text{water}}$ and $\delta^2$H) were measured using a Picarro L2120-i near-infrared Cavity Ring Down Spectrometer (IR-CRDS) with High Precision Vaporizer A0211. Results of water analyses are reported on the VSMOW (Vienna Standard Mean Ocean Water) scale. The reproducibility of the $\delta^{18}$O$_{\text{water}}$ and $\delta^2$H results is ±0.1‰ and ±1‰, respectively. Correlations between $\delta^{13}$C$_{\text{carb}}$ and $\delta^{18}$O$_{\text{carb}}$ profiles were evaluated using Spearman’s rank-order correlation ($n = 31$).

Ordination analysis

The statistically significant zones of major change in sedimentary pigments were identified using a stratigraphically constrained incremental sum-of-squares clustering (CONISS) analysis based on a Euclidean dissimilarity matrix and a broken stick model from the vegan package in R (Juggins 2009). The pollen zones were defined with the aid of a Constrained Incremental Sum of Squares (CONISS) cluster analysis included in the TILIA program (Grimm 1993). The numbers of statistically significant zones were determined using a broken stick model for all pollen taxa. All ordination analyses were performed on normalized data sets; sedimentary pigments were log-transformed and pollen percentages were square-root transformed.

Results

Age-depth model and sediment lithology

$^{210}$Pb activity in core V94 showed a monotonic decrease down the sediment profile with subtle variation between 30–45 cm depths (Fig. 2a). The $^{210}$Pb/$^{226}$Ra equilibrium was reached at a depth of 55 cm. The mean $^{210}$Pb flux (of 109 Bq m$^{-2}$ y$^{-1}$) calculated from the total inventory in the sediment core complied with expected atmospheric input at this geographic location (Realo et al. 1995). The $^{137}$Cs activity, measured throughout the core profile, showed a clear peak at 25 cm (maximum activity of 75 Bq kg$^{-1}$). We also detected $^{241}$Am in the same interval. The $^{137}$Cs/$^{241}$Am ratio (not shown) indicated that the $^{137}$Cs peak was caused by atmospheric deposition during the 1963 peak in Nuclear Weapon Testing (NWT) era (Appleby et al. 1991). Lake Verevi is a site with a century-long disturbance that resulted in changes in the sedimentation dynamics (Vandel and Koff 2011). Hence, the radiometric dates and variation in sedimentation rates were established using a constant rate of supply (CRS) model which accounts for the variation in sediment accumulation rates. The use of CRS-modelled $^{210}$Pb age-depth profiles was validated by the reference time marker (i.e., the $^{137}$Cs NWT fallout peak) which was in a close agreement with the CRS-modelled $^{210}$Pb dates (Fig. 2b). The sediment accumulation rates (SAR) were stable (0.02 g cm$^{-2}$ y$^{-1}$) until the 1930s (Fig. 2b). From the 1930s to the 1950s, SAR accelerated twofold (0.05 g cm$^{-2}$ y$^{-1}$) and continued to gradually increase to a peak in the 1990s (up to 0.07 g cm$^{-2}$ y$^{-1}$).
The age-depth stratigraphy of V96 core was inferred from the dated core V94 by comparing their lithological features (Fig. 3). We inferred that the shift from mineral- to carbonate-rich sediments at ~34 cm in core V96 occurred in the late 19th century (ca. 1880). The first peak in carbonate content (29 cm; core V96) was dated to ~1909 and the second broad peak (~20–10 cm; core V96) was assumed to represent the period between the 1960s–1990s. Due to the inherent uncertainties of the approach, the age-depth stratigraphy of core V96 should be considered as an auxiliary reference. Rather, the paleolimnological analysis based on the indicators from core V96 focused on the reconstruction of the major recorded events that occurred during the 20th century as opposed to reconstructing finer, decadal-scale dynamics.

The lithological composition of the two sediment cores, V94 and V96, were very similar with an approximate 3–5-cm lag among the main lithological points (Fig. 3). The sediment
The CONISS analysis identified three main zones in the pigment record (Fig. 4). The lutein-zeaxanthin complex (green algae-cyanobacteria) and β-carotene (total phytoplankton production) dominated the sediment core, but all pigments experienced an accelerated increase at the turn of the 19th century (Z2). Pigment concentrations remained high thereafter (Z3), to the exception of echinenone which oscillated irregularly over the last ca. 100 years. Most recently (ca. 1990), echinenone, Chl a and lutein-zeaxanthin declined, whereas canthaxanthin (a cyanobacteria-specific pigment) and β-carotene reached maximum concentrations in the surface sediment layers. The ratio of Chl a to pheophytin a (preservation index) was largest in zone Z1 and decreases in zones Z2 (19th century) and Z3 (post 1900s).

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**Pediastrum remains and pollen**

The pollen stratigraphy was divided into four statistically distinct zones (CONISS analysis; Fig. 5), which broadly agreed with the pigment zonation. The lowermost zone (V1; 70–44 cm; pre-19th century) was characterized by a high proportion of Betula (up to 60%), and pollen grains from the Pinus, Picea and Alnus trees. Poaceae values were low (3%) and only a few pollen grains of ruderals and rye (Secale) were found at this time. The subsequent zone (V2; 44–30 cm; 19th century) experienced a notable
decrease in the Betula pollen and fluctuating values of Pinus. This zone also showed a slight increase in Poaceae, and maximum values of the Secale grains (up to 2%) and the Pediastrum remains. The 20th century (zone V3; 30–8 cm) was characterized by stable values for Pinus, Betula and Alnus and an increase in Salix and ruderals. The proportion of the Poaceae pollen remained high as well. In contrast, there was a sharp decrease in Pediastrum values. The uppermost zone (V4; 8–1 cm; ca. last 20 years) showed a slight increase in the content of all tree pollen and a decrease in grasses, ruderals and rye. Only pollen of Urtica and Plantago sporadically appeared in higher values while, in the same time Pediastrum continued to decrease.

Stable isotopes

The stable carbon (δ13Ccarb) and oxygen (δ18Ocarb) isotopes were found from samples above 60 cm, where the carbonate content in the sediment exceeded 7% (Fig. 6). The δ13Ccarb and δ18Ocarb profiles were strongly positively correlated (Spearman’s r = 0.88, p = 0.0000002) and values varied over a range of 7‰ (carbon) and 6‰ (oxygen). The δ13Ccarb signature was low below 45 cm (between –6‰ and –9‰) and increased thereafter (over last ca. 200 years). The highest δ13Ccarb values (–1‰) occurred between ca. 1970 and 1990 (17–9 cm), and decreased strongly in recent years (to –5‰ in surface layers). Similarly, a clear increase in stable oxygen isotopes commenced at 45 cm; reaching their highest values in the 1970s (17 and 15 cm; –7‰). The δ13Ccarb and δ18Ocarb peaks corroborated with maximum rates of carbonate accumulation (Figs. 3 and 6). The δ18O showed more positive values in epilimnetic waters compared to the hypolimnetic waters and mean annual precipitation values (–10.4‰; Table 1; Punning et al. 1987).
Discussion

Relationship between anthropogenic change and inferred water quality

Based on historical and limnological surveys we hypothesized that one of the main drivers of the recent eutrophication of Lake Verevi was the development of the city of Elva on the lake’s shore at the start of 20th century (Table 2). In the 1930s, recreational facilities were built and the lake became increasingly popular among vacationers, thereby increasing the pressure to the lake’s ecosystem state. Indeed, the first eutrophication signal identified in the limnological survey dated back to 1929. At this time, the lake was moderately eutrophic, the water column was stratified and bottom waters were near anoxic (Riikoja 1940). The first phytoplankton samples, collected in 1928, were also indicative of eutrophic conditions, with assemblages dominated by large green algae (i.e. *Pediastrum*, *Staurastrum* spp. and *Botryococcus*) and chrysophytes. Cyanobacteria (*Anabaena* spp.) were likewise recorded at this time.

A second known cause of eutrophication in Lake Verevi is the historical increase in nutrient load from urban wastewaters. To accommodate an increasing population, oxidation ponds were constructed at the end of the 1970s near the lake’s shore (0.5 km) to process the urban wastewaters. These ponds were connected to the lake and are believed to have pushed the lake into a hypereutrophic state in the 1980s (Ott et al. 2005). By the late 1980s, the town’s wastewater treatment plant began operations (Järvet 1989), however, ongoing episodic discharges from old oxidation ponds kept the lake in a high nutrient state, as evidenced by the reported appearance of the cyanobacteria *Oscillatoria* spp. (Milius 1989). In 2002, oxidation ponds were isolated by dams, ceasing the pollution to the lake (Table 2).

Paleolimnological data, such as sedimentary pigments and $\delta^{13}C_{\text{carb}}$, were in strong agreement...
with the long-term changes in water quality measured within the water column. For instance, echinenone and canthaxanthin tracked the rise in total and colonial cyanobacteria, respectively. Sedimentary pigments further identified a period of increased production beginning in the 20th century, which peaked between 1970 and 1990. This increase was in strong agreement with the eutrophication of Lake Verevi. The slight time lag between paleolimnological and monitoring data are likely due to the intermittent sampling of the lake surveys program. Also, carbonate precipitation reached maximum values in the 1980s, and the most positive values of $\delta^{13}$C$_{\text{carb}}$ and $\delta^{18}$O$_{\text{carb}}$ occurred between 1970 and 1990. Decreasing values of $\delta^{13}$C$_{\text{carb}}$ and concentrations of several pigments (Chl $b$, echinenone and lutein-zeaxanthin) in the uppermost core intervals most likely indicated the stabilization or recovery of the lake in the last ten years. This corresponds with the isolation of old oxidation ponds by dams (Table 2).

### Response of $\delta^{18}$O$_{\text{carb}}$ to other proxies

The $\delta^{18}$O$_{\text{carb}}$ profile of Lake Verevi appeared to be directly related to other proxy records. The strong positive correlation between $\delta^{18}$O$_{\text{carb}}$ and $\delta^{13}$C$_{\text{carb}}$ is poorly understood, however, the covariance between $\delta^{13}$C$_{\text{carb}}$ and $\delta^{18}$O$_{\text{carb}}$ has frequently been used as an indicator of lake hydrol-

<table>
<thead>
<tr>
<th>Year</th>
<th>Historical records</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1889</td>
<td>Railway was built</td>
<td>Suur 1973</td>
</tr>
<tr>
<td>1929</td>
<td>Stratified, moderately eutrophic</td>
<td>Riikoja 1940</td>
</tr>
<tr>
<td>1930s</td>
<td>Swimming pool was built, ~2000 summer guests and same number of local residents</td>
<td>Kärner 1931, Ott et al. 2005</td>
</tr>
<tr>
<td>1957</td>
<td>Stratified, eutrophic</td>
<td>Mäemets 1968</td>
</tr>
<tr>
<td>1978</td>
<td>On the inflow ditch to the lake, several oxidation ponds were built</td>
<td>Ott et al. 2005</td>
</tr>
<tr>
<td>1980s</td>
<td>Strong algal blooms, anoxia in whole water body in winter</td>
<td>Timm 1991, Ott et al. 2005</td>
</tr>
<tr>
<td>1984</td>
<td>Hypertrophic lake</td>
<td>Milius 1989</td>
</tr>
<tr>
<td>1988</td>
<td>Wastewater treatment plant was built</td>
<td>Järvet 1989</td>
</tr>
<tr>
<td>1990s</td>
<td>~20000 summer guests</td>
<td>Timm 1991</td>
</tr>
<tr>
<td>1998</td>
<td>Cleaning of the lake beaches, water level drop by 0.7 m</td>
<td>Ott et al. 2005</td>
</tr>
<tr>
<td>2002</td>
<td>Inflow from oxidation ponds closed</td>
<td>Ott et al. 2005</td>
</tr>
</tbody>
</table>

More commonly, when lake carbonates precipitate close to the isotopic equilibrium of ambient water, the stable oxygen isotope composition in authigenic carbonates has been suggested to be a proxy for paleo-precipitation and eutrophication (Fritz et al. 1987, Leng et al. 2005). This interpretation has been refuted by several authors who have shown that in eutrophic waters, calcite precipitation is in disequilibrium and the oxygen ratio is more depleted than when precipitation occurs in equilibrium with the ambient water (Fronval et al. 1995, Teranes and McKenzie 1999, Jinglu et al. 2004). The higher values of $\delta^{18}$O$_{\text{carb}}$ identified in Lake Verevi, were likely influenced by additional factors, such as metabolic fractionation and photosynthesis (both of which are important sources of oxygen) and mineralogy. Furthermore, anthropogenic changes in the catchment, such as the construction of oxidation ponds, coincided with the period of oxygen isotope over-enrichment. Waters from these ponds were often
driven by floods into the lake, carrying nutrients and possibly more positive $\delta^{18}O_{\text{water}}$.

In summary, although we cannot discount the climatic influence on the isotopic signature of Lake Verevi, eutrophication had a greater effect than previously believed. The significant correlation between $\delta^{13}C_{\text{carb}}$ and $\delta^{18}O_{\text{carb}}$ suggests that CaCO$_3$ precipitation induced by algal photosynthesis and increasing pH strongly affected $\delta^{18}O_{\text{carb}}$. Therefore, our multi-proxy study clearly demonstrates that in-lake processes, such as increased biological production, may drive $\delta^{18}O_{\text{carb}}$ enrichment. If $\delta^{18}O_{\text{carb}}$ was controlled by climate alone, the enrichment in some sediment intervals would not have been as elevated. The composition of stable isotopes is complex and understanding environmental processes that lead to isotopic variations in lake carbonates requires further work.

Response of proxies to anthropogenic change prior to limnological surveys efforts

Based on our results, the first eutrophication signal occurred at the start of the 19th century, as indicated by the sharp rise in *Pediastrum* spp., enriched $\delta^{13}C_{\text{carb}}$ values and the increase in pigment concentrations (e.g. echinenone and Chl $a$; Figs. 5 and 7). The increase of Poacea also suggests an opening of the landscape at this time. The concurrent rise in the *Secale* pollen and upland herbs indicate the intensification of agricultural activities (Fig. 5). These changes coincide with the historical period when peasants obtained the right to buy land in the mid-19th century, resulting in an increase in agricultural land use (Rosenberg 2013). Thereafter, *Pediastrum* spp. decreased and cyanobacteria pigment concentrations increased, which suggests continued ecological changes in the lake. These results are consistent with paleolimnological studies by Heinsalu and Alliksaar (2005) from Lake Verevi, where the early 19th century eutrophication signal was identified by diatom inferred total phosphorus concentrations (DI-TP) (Heinsalu and Alliksaar 2005). 1 = establishment of a swimming pool in the lake, 2 = establishment of oxidation ponds near the lake, 3 = decreased water level during cleaning of beaches, 4 = inflow to the oxidation ponds near the lake closed.

Fig. 7. Changes in *Secale* and *Pediastrum*, sedimentary pigment preservation conditions (chlorophyll $a$ / pheophytin $a$), cyanobacteria pigments (g$^{-1}$ OM), stable $\delta^{13}C_{\text{carb}}$, the sediment content as loss on ignition (LOI) and diatom inferred lake total phosphorus concentration (DI-TP) (Heinsalu and Alliksaar 2005). 1 = establishment of a swimming pool in the lake, 2 = establishment of oxidation ponds near the lake, 3 = decreased water level during cleaning of beaches, 4 = inflow to the oxidation ponds near the lake closed.

The rise of *Secale* confirms our assumption that the significant changes in land use occurred at the same time as forest clearance and the drainage activities, during which the outflow ditch to the Kavilda River was dredged to drain the boggy catchment area for agriculture. We assume that this dredging also caused the mid-19th century drop in water level.
Preservation of sedimentary pigments

The degradation of pigments during sedimentation has been argued to affect the reliability of pigments as proxies of changes in the algal community. However, in Lake Verevi the preservation of sedimentary pigments, measured as the ratio of Chl \( a \) to pheophytin \( a \), was high (Fig. 7) and peaks prior to the 1850s, following the increase in cyanobacteria concentrations and total production markers (Figs. 4 and 7). As reviewed in Leavitt and Hodgson (2001), the preservation of pigments during the sedimentation process is tightly linked to the lake trophic state. Therefore, the increased productivity in Lake Verevi led to improved preservation conditions for pigments (i.e. diminishing water visibility, lower oxygen levels and rapid sedimentation). Prior to the 1850s, the preservation of pigments was better than later, even during the lake’s hypereutrophication period in the 1980s, which suggests that preservation conditions may have changed substantially in the 1850s. Based on our paleolimnological data (i.e. sedimentary pigments, \( \delta^{13}C_{\text{carb}} \), Pediastrum spp.), we infer that the lake trophic state continuously increased from the 1850s, which should lead to progressively better preservation of pigments (Fig. 7). Yet, instead, the ratio of Chl \( a \) to pheophytin \( a \) showed the deterioration of pigment preservation. Therefore, it is probable that during the mid-19th century, Lake Verevi underwent a water level drop, resulting in a more oxygenated surface sediment in the shallow regions of the lake, and consequently, an increased degradation of sedimentary pigments. This is consistent with the mid-19th century land use changes by dredging, which could be a cause of the water level drop in Lake Verevi. We also suggest that the recent, 20th century, drop in water level (to 0.7 m; Ott et al. 2005) strongly influenced sedimentary pigments from the littoral zone, causing the observed decrease in several pigment markers (e.g. echinenone and Chl \( a \)).

Conclusions

The study of the response of lake ecological status to environmental change is usually limited to recent decades, precluding a complete evaluation of historical changes that have taken place since the start of major anthropogenic change. The aim of this study was thus to reconstruct long-term (last ca. 200 years) changes in water quality proxies and evaluate whether the dynamics of selected proxies reflect changes in lake status measured within the water column. We used three independent paleo-indicators to describe and quantify the water quality of the hard-water Lake Verevi, where a combination of several human activities and untreated wastewater inflows caused an accelerated eutrophication signal leading to massive algal blooms and the depletion of oxygen in bottom waters. Combining the information from past limnological surveys and sedimentary records allowed us to precisely describe the process of lake eutrophication and confirm its anthropogenic drivers at a time when historical data were not available.

The multiple sediment core proxies examined here (i.e. sedimentary pigments, \( \delta^{13}C_{\text{carb}} \), \( \delta^{18}O_{\text{carb}} \) and remains of the green algae Pediastrum spp.) tracked important changes in lake productivity that corroborated with contemporary lake monitoring data. In addition, sedimentary pigments and stable isotopes identified short, periodic changes in lake productivity beginning in the 19th century that were in direct response to human impact which preceded the start of the monitoring program. These changes in lake productivity and human impact also coincided with the timing of peaks in green algae remains. Lastly, pigment preservation, often argued to be a caveat of the sedimentary pigment approach, offered valuable supplementary information on lake level changes and sedimentation conditions. In particular, the ratio of chlorophyll \( a \) to pheophytin \( a \) clearly responded to the first increase in trophic status at the start of the 19th century, whereas the subsequent decrease in pigment preservation was attributable to the drop in lake water level.

Eutrophication increasingly threatens the resilience of lake ecosystems and their ability to recover to baseline conditions (Søndergaard et al. 2007). Based on the study of twelve European lakes, Bennion et al. (2015) concluded that lake recovery is a lengthy process where the outcomes can be quite variable among lakes,
notably so in shallower sites. Ongoing climate change is likely to lead to unprecedented interact with eutrophication as well as local, site-specific factors (internal loading or land-use change), potentially confounding or even preventing lake recovery to historical conditions. Nevertheless, our study showed that lakes might stabilize after a prolonged and strong eutrophication pressure. Analogous trajectories of change have been observed in numerous European lakes impacted by cultural eutrophication. For instance, Jeppesen et al. (2007) observed that majority of lakes responded to restoration measures, especially to significant reductions in nutrient loading. Yet, in some cases the improvement was short lived mainly due to the internal loading of phosphorus. Considering the century long impact of eutrophication in Lake Verevi, such scenarios remain a possibility, and continued monitoring of nutrient dynamics must remain a priority of the lake’s management program. Our findings highlight that paleolimnological assessment of ecological change over decad to centennial timescale is key to setting realistic management and restoration targets. Similarly, our study shows that using multiple indicators are needed to evaluate a wider range of ecosystem responses to environmental stressors, and that multi-proxy paleolimnological techniques (pollen, sedimentary pigments, stable isotopes) have an important role to play in future studies of degradation and recovery pathways of shallow lakes.

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